



Mercury diffusion in gold and silver thin film electrodes on quartz crystal microbalance sensors[☆]

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ABSTRACT

Diffusion behavior of mercury into both gold and silver electrodes of polished and roughened quartz crystal microbalances (QCMs) is presented. Several QCM devices were exposed to mercury vapor for 8 h and allowed to desorb for 5 h under controlled nitrogen atmosphere. The process was repeated for different Hg concentrations of 1.02, 1.87 and 3.65 mg/m³ at an elevated temperature of 40 °C. The chemical composition and surface morphology of each QCM surface was characterized by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS), Secondary Ion Mass Spectroscopy (SIMS), Atomic Force Microscope (AFM) and Field Emission Secondary Electron Microscope (FE-SEM). The Ag electrodes were found to contain up to 16% more adsorbed/amalgamated Hg by mass than the Au samples. It was found that the ratio of amalgamated to adsorbed Hg is less for Au than Ag. SIMS analysis confirmed high Hg diffusion through rough substrates, 40 days after Hg exposure. In situ sticking probability of the tested mercury vapor concentrations to Au and Ag surfaces at 40 °C was found to drop at quicker rates than the reported Hg–Au and Hg–Ag room temperature values. Overall, in the context of Hg vapor phase gas sensing applications, the rougher gold substrate was found to outperform the other samples due to its superior adsorption/desorption properties.

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1. Introduction

The adsorption and desorption of Hg on noble metal thin films is the basis of many commercial Hg vapor sensors [1]. The ability for gold to absorb and amalgamate mercury is well known [2]. Quartz crystal microbalance (QCM) transducers, with gold thin film electrodes have shown good potential to be used as Hg vapor sensors in air [3], and were first used as a Hg vapor sensor in 1974 [4]. QCMs are thought to be well suited for many different types of sensing applications due to their unique combination of mechanical, electrical, chemical and thermal properties, which have led to their commercial significance [5]. QCMs have also been used for etching studies, thin film deposition control and estimation of stress effects [6]. It is a well understood process that upon addition of mass (Δm) at the electrode surface of a QCM, the resonant frequency (f_0) is perturbed, which results in a measurable frequency shift, (Δf). By analytically solving the one-dimensional equation of motion, Sauerbrey showed that for an ideal layer of foreign mass (Δm) deposited on the surface

of a QCM the frequency change (Δf) is given by:

$$\Delta f = -\frac{2f_0^2}{A\sqrt{c_{66}\rho_q}}\Delta m = -S_f\Delta m, \quad (1)$$

where S_f represents the integral mass sensitivity (or Sauerbrey constant) and is proportional to the square of the fundamental frequency, f_0 , inversely proportional to the surface area, A , and increases proportionally with the overtone number [6]. The material properties of the quartz are defined by c_{66} and ρ_q . Interaction mechanisms of noble metals such as gold and silver with mercury vapor have been studied in some detail. Kalb [7] has showed that Ag amalgamates well with Hg, while Be'er et al. [8] studied the diffusion of liquid Hg through solid Ag and reported the formation of Ag₃Hg₄ and Ag₄Hg₃ amalgams. It has been shown by Battistoni et al. [9] that low vapor Hg concentration is adsorbed only by the first 5–6 nm sub-layer of a thin gold film, while George and Glaunsinger [10] found that the film morphology is critical for an optimum thin film sensor response to Hg, and proposed that the rougher, more porous films promote diffusion of the mercury into the films' grain boundaries and into the gold bulk. The diffusion coefficient of Au–Hg system at room temperature has also been investigated in the past and is reported to be $\sim 1.14 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ [11]. A model developed by Levlin et al. [12] explains the adsorption and diffusion of Hg into Au and Ag (1 1 1) surfaces based on scanning

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tunnelling spectroscopy (STM) results. This work was instrumental in showing that the saturation level of adsorbed Hg is dependent upon the concentration in the carrier gas, i.e. upon temperature and the flux of Hg atoms at the surface. The proposed model suggested that Hg diffusion into the Au/Ag films is not a major factor. To our knowledge, too little attempt has been made to estimate gaseous Hg diffusion through Au and Ag thin films quantitatively. In this work we present an investigation to compare Hg adsorption, desorption, amalgamation, diffusion and sticking probability on gold and silver thin films deposited on optically polished and roughened quartz substrates. An optimum substrate for Hg vapor sensing is nominated from the four studied substrate types, based on Hg diffusion data, Au–Hg sticking probability and QCM dynamic response data.

2. Experimental

Eight 10 MHz QCM resonators, four of which were optically polished and the other four had mechanically roughened faces, were purchased from Hy-Q crystals, Victoria, Australia. Thin films of Au and Ag of 115 nm thick were deposited as the QCM electrodes by thermal evaporation at room temperature. Analytical grade HNO_3 , HCl , H_2SO_4 and KMnO_4 were purchased from Aldrich and Hg permeation tubes were purchased from VICI, TX, USA. Using a PID temperature controller at different set points to heat the permeation tubes, different Hg concentrations were generated. Each Hg concentration was calibrated using KMnO_4 trapping method at the point where the gas enters the cell housing the QCMs. The Hg trapped in the $\text{KMnO}_4/\text{H}_2\text{SO}_4$ solution was quantified using Agilent Technologies HP4500 series 300, ShieldTorch system ICP-MS.

The QCM resonant frequency change, Δf was measured using an Agilent (53131A) frequency counter. Each QCM was tested at three Hg concentrations of 1.02, 1.87 and 3.65 mg/m^3 (balance N_2), all at constant temperature of 40°C and constant flow rate of 200 sccm using specially developed 4 channel mass flow controller system. The approximate volume of the chamber housing the QCM sensors was $\sim 0.5 \text{ L}$. The QCM sensors were not subjected to any pre-treatment before being exposed to Hg vapor for 8 h and allowed to desorb for 5 h under controlled nitrogen atmosphere. It was determined, from preliminary experiments with extended desorption times, that the desorption of Hg beyond the initial 5 h time period is minimal, thus justifying the chosen 5 h desorption time used in the experiments. This also indicates that a given amount of Hg is never released from the surface, which is evident from the baseline shift between $t = 0$ and $t \sim 800 \text{ min}$ in Fig. 4A and B.

In order to estimate the remaining amalgamated/adsorbed Hg content on the Au and Ag electrode surfaces, four QCM devices were digested in aqua regia (1:3 concentrated HNO_3 : HCl) directly following their removal from the chamber. The solution was then analysed by ICP-MS to determine the remaining Hg content which either diffused into the bulk or was strongly amalgamated. The remaining samples were tested under identical conditions and then characterized by AFM, FE-SEM and SIMS. QCM results revealed good repeatability of $\pm 0.6\%$ in response magnitude between duplicate tests and of similar substrates. AFM measurements were performed with a NanoScope IIIa Multimode AFM (Digital Instruments, USA) in tapping mode at room temperature and relative humidity of 40%. MikroMasch Ultrasharp (NSC15/A1 BS) silicon etched SPM probes with reflective Al coating on the backside, spring constant of 40 N/m , the tip radius of curvature $< 10 \text{ nm}$ and resonant frequency of 325 kHz were used. FE-SEM imaging was performed on a high resolution Nova FE-SEM. SIMS (Cameca IMS 5f, France) depth profiles were performed 40 days after the controlled Hg vapor exposure using a Cs^+ primary ion beam of 3 keV net impact energy, 1.5 nA beam current and a raster area of $500 \mu\text{m} \times 500 \mu\text{m}$. To eliminate potential edge effects, a combination of lens setting was used to

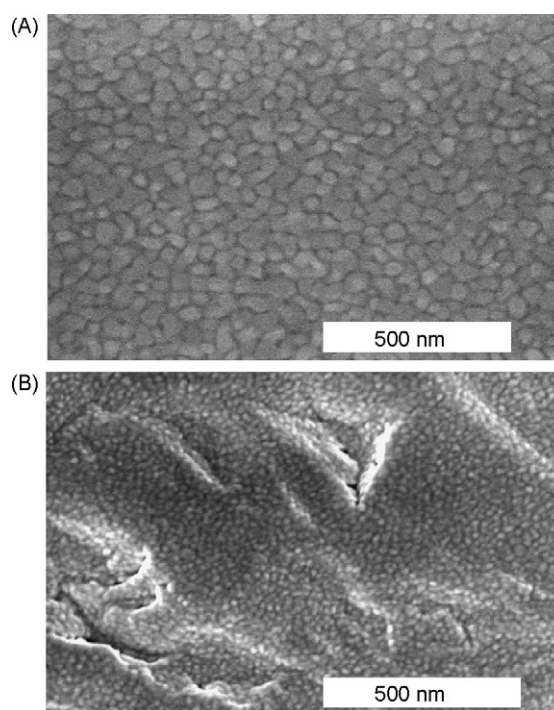


Fig. 1. SEM images of (A) Au-polished and (B) Au-rough quartz crystal surfaces.

restrict the secondary ion yield to a $100 \mu\text{m}$ diameter region within the centre of the rastered area.

3. Results and discussions

The FE-SEM micrographs of the gold coated polished and roughened quartz is shown in Fig. 1. The Au-polished and Au-rough AFM images detailing the average roughness (R_a) and root-mean-square roughness (R_q) over a $500 \text{ nm} \times 500 \text{ nm}$ scan size is shown in Fig. 2A and B, respectively. Similarly, the AFM images of Ag-polished and Ag-rough substrates are shown in Fig. 3A and B, respectively. The AFM measurements revealed the Au-polished QCM electrodes have a 4.75% larger surface area than its projected surface area. Similarly Au-rough, Ag-polished and Ag-rough were found to have 18.9, 7.7 and 41.8% higher surface area than their projected surface areas. Although the AFM image of the gold coated polished substrate appears to have smaller gold grain sizes, the much larger features of the roughened substrate are formed of many smaller gold grains that follow the topology of the underlying roughened quartz. These smaller gold grains can be clearly observed in the SEM images and were not well resolved by AFM. However, it is expected that the roughened QCM crystals will have higher response towards Hg vapor than their polished counterparts mainly due to their higher surface areas and smaller grain sizes which would result in many more grain boundaries and possibly more defect sites.

3.1. ICP-MS and QCM results

The dynamic response of four QCM devices, namely, Ag-polished, Au-polished, Ag-rough and Au-rough electrode QCMs towards 3.65 and 1.02 mg/m^3 of Hg vapor are shown in Fig. 4A and B, respectively. The QCM responses towards Hg vapor show the Au-rough to exhibit the highest response magnitude even though the Ag-rough has 19.3% higher surface area than the Au-rough QCM. Similarly, Au-polished QCM is found to have larger response magnitude than the Ag-polished substrate, although having lower surface

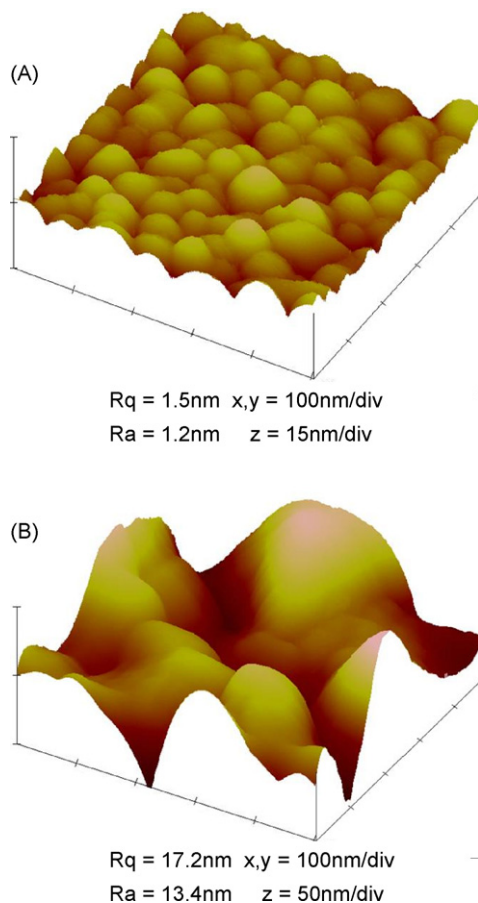


Fig. 2. AFM images of (A) Au-polished and (B) Au-rough quartz crystal surfaces.

area than the Ag-polished counterpart. The ICP-MS and QCM results obtained are summarized in Table 1. The adsorption and desorption rates for the initial 2 min are reported. The initial rate of adsorption is observed to be the largest for the Au-polished. However, during the desorption phase (time >550 min), the Au-rough is found to dominate. At the end of 8 h Hg exposure period, the Ag-rough and Au-rough were observed to adsorb a larger quantity of Hg than their respective polished counterparts, with Au-rough sample having adsorbed 5% more Hg than the Ag-rough. The highest desorption rate occurred on the Au-rough and Ag-rough substrates with the Au desorbing at more than double the rate of Ag in the initial 2 min desorption period (see bold values in Table 1).

The higher desorbing property of gold was confirmed when the samples were immediately digested following the 5 h desorption period, and analysed by ICP-MS. The total Hg content in the Ag-rough substrates was found to be 16% by mass more in comparison to the Au-rough QCM, indicating Ag retained more Hg than the gold surfaces even after the 5 h desorption period. The results show that Hg desorption occurs faster from both the Au-polished and Au-rough QCMs than the Ag counterparts. The high desorption ability indicates that gold is the better candidate for Hg sensing applications.

Table 1
QCM adsorption/desorption data of Hg on Au-/Ag-rough and Au-/Ag-polished thin films.

Sample	Adsorption rate ($\mu\text{g cm}^{-2} \text{ min}^{-2}$)	Total adsorbed ($\mu\text{g cm}^{-2}$)	Desorption rate ($\mu\text{g cm}^{-2} \text{ min}^{-2}$)	Total desorbed ($\mu\text{g cm}^{-2}$)	ICP-MS ($\mu\text{g cm}^{-2}$)
Ag-polished	0.079	3.000	0.016	1.290	0.775
Au-polished	0.213	3.320	0.020	1.460	0.706
Ag-rough	0.087	5.190	0.024	1.940	1.380
Au-rough	0.160	5.450	0.050	2.440	1.190

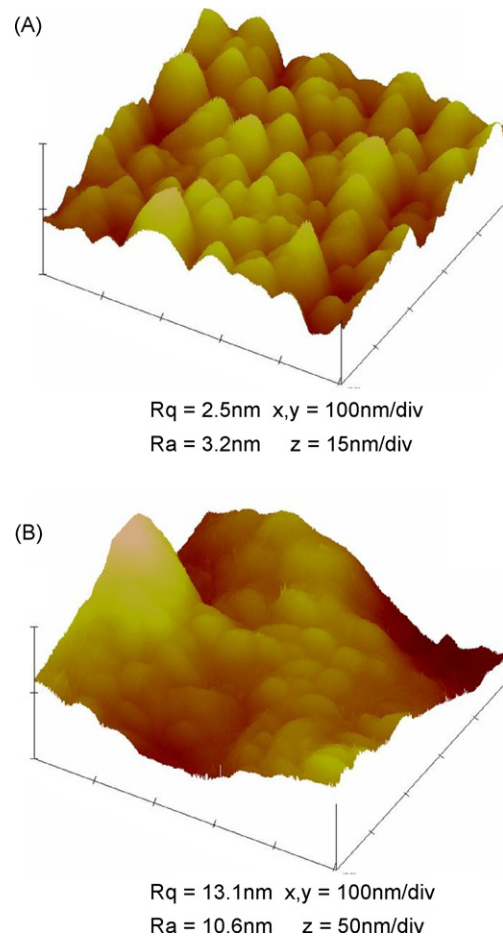


Fig. 3. AFM images of (A) Ag-polished and (B) Ag-rough quartz crystal surfaces.

Regarding sensor design, the response time of the QCM based sensors is also an important parameter. For most applications a short response time indicates higher affinity towards the analyte. The required time for an analyte to adsorb or desorb from the substrate have been reported to depend on the diffusion coefficient of the analyte in the substrate [13]. The t_{90} parameter is used within the sensor community to define the time required to obtain 90% of the intensity of the equilibrium value for a given adsorption or desorption phase of a sensing process. For the adsorption phase of the Au-rough QCM (Fig. 3A), the t_{90} was found to be the fastest, having reached 90% of the surface saturation within 93 min after exposure to 3.65 mg/m^3 of Hg. Similarly, the t_{90} for Au-polished, Ag-rough and Ag-polished were found to be 134, 263 and 230 min, respectively. Surprisingly, all four samples had equal desorption t_{90} of $191.5 \pm 1 \text{ min}$. For the lower Hg concentration of 1.02 mg/m^3 (Fig. 3B), the adsorption t_{90} for Au-Rough and Au-polished had increased by 50 and 100%, respectively. However, the adsorption t_{90} for Ag-rough and Ag-polished had increased by around 5% each. Although the t_{90} response times are well known to be analyte concentration dependent, this study gives an insight into the practicality of employing Ag and Au thin films as sensitive layers for

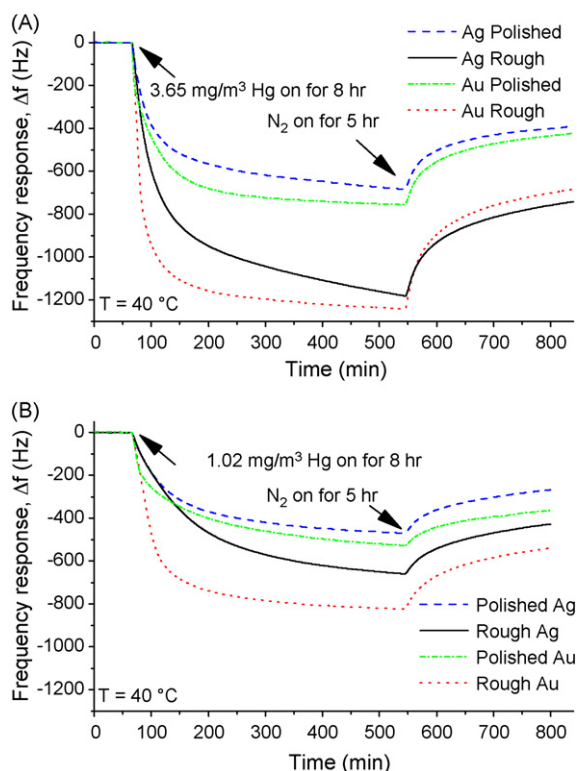


Fig. 4. Sensor response of the Au-/Ag-polished and Au-/Ag-rough thin film QCMs exposed to (A) 3.65 mg/m^3 and (B) 1.02 mg/m^3 of Hg for 8 h followed by N_2 for 5 h at 40°C (constant flow rate of 200 sccm).

Hg sensor applications. It is well known that with higher analyte concentrations much lower t_{90} are obtainable [14].

Diffusion is well known to be the process by which matter is transferred from a region of higher to that of lower concentration in the system as a result of random molecular motions [15]. The extent of depth to which Hg has diffused through the Au or Ag thin film is dependent on the difference between the total amount of Hg adsorbed during the initial exposure and the desorbed quantity during the controlled 5 h desorption period. This difference has been obtained from the QCM data and confirmed with ICP-MS as shown in the last column of Table 1. It was observed that ICP-MS repeatedly showed lower Hg content in each sample as compared to the QCM data derived from the Sauerbrey equation. This discrepancy may be due to some further uncontrollable desorption of Hg content while placing the device in the digestion solution directly after the 5 h desorption phase of the experiment. That is, some of the adsorbed elemental Hg is expected to not digest/oxidize well in Aqua regia, as opposed to Au, and may evaporate during the digestion process. Acidic permanganate solutions and Hopcalite based catalyst adsorbent tube are widely used and have been adopted as official assessment methods for oxidizing elemental Hg vapor that may be desorbed off the sample surface [16–18]. However, with the current digestion method used, the ICP-MS results conclusively confirm the lower mercury content in Au samples as compared to Ag substrates, regardless of the substrate morphology.

3.2. SIMS diffusion study

The QCM samples that were set aside for SIMS characterization were analysed 40 days after their exposure to Hg. The samples were stored in air at room temperature during the 40-day period. The SIMS depth profiling shown in Figs. 5 and 6 are for the samples which were exposed to 3.65 mg/m^3 Hg at 40°C (Fig. 4A). The SIMS data clearly show that Hg diffuses deeper into the Au-rough sub-

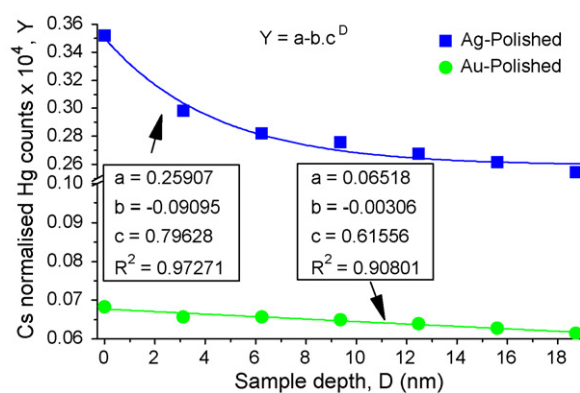


Fig. 5. SIMS depth profile for polished Ag and polished Au thin film QCM electrodes.

strate. The results presented are inline with the conclusions made by George and Glaunsinger [10], indicating that the Hg vapor nucleates and diffuses better at surfaces with more grain boundaries, thus showing that the rough surfaces do indeed provide a higher concentration of adsorption sites. Therefore the extent of roughness of the material used as the sensing layer for Hg adsorption is suggested as the dominant factor in the extent of diffusion/amalgamation that occurs.

The depth profiles showed that from the 4 different surface configurations, the least amount of Hg diffusion occurred through the Au-polished sample. This further supports the mass change calculated from the Sauerbrey equation and the ICP-MS results (Table 1) showing that the silver samples retain the larger proportion of the adsorbed Hg content when compared to the Au QCMs.

The trend lines (Figs. 5 and 6) were fitted to the data points using best line of fit method. These fitted lines are found to best follow the asymptotic Eq. (2):

$$Y = a - bc^D, \quad (2)$$

where Y is the normalized Hg count, parameters a , b and c are constants, and D is the surface depth at which Hg has diffused through. Due to a lack of SIMS Au–Hg reference materials, the normalized Hg counts were not quantified. The parameters a , b and c for the three different Hg concentrations on the four different substrate configurations are shown in Table 2. The right side of Eq. (2) is indicative of the extent of diffusion occurring in a substrate while the parameter a on the left indicates the flux/counts of Hg in the substrate where no further diffusion occurs. A high a value indicates the lower ability of Hg diffusion in the substrate. Due to the low QCM response for Ag-polished substrates and high diffusion observed in Fig. 5, it is clear that Ag retains more of the adsorbed Hg than the Au films. The lower t_{90} and higher desorption rate observed for Au-polished than

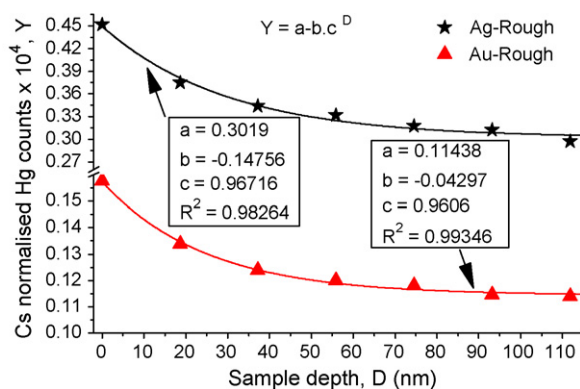


Fig. 6. SIMS depth profile for rough Ag and rough Au thin film QCM electrodes.

Table 2
Parameters *a*, *b* and *c* (to three decimal places) for Eq. (2).

Sample	1.02 mg/m ³ Hg			1.86 mg/m ³ Hg			3.65 mg/m ³ Hg		
	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>	<i>a</i>	<i>b</i>	<i>c</i>
Ag-polished	0.041	0.000	0.000	0.057	0.000	0.000	0.259	−0.091	0.796
Au-polished	0.041	0.000	0.000	0.058	0.000	0.000	0.065	−0.003	0.616
Ag-rough	0.274	−0.191	0.970	0.224	−0.163	0.971	0.302	−0.148	0.967
Au-rough	0.085	−0.029	0.972	0.068	−0.041	0.985	0.114	−0.043	0.961

the Ag-polished may be due to lower Hg diffusion in the gold substrate observed in Fig. 5. This may in turn be due to the initial lower Hg concentration on the surface before the substrates were left for 40 days prior to SIMS analysis. The higher *a* values observed for Ag substrates over the Au is a clear indication that diffusion is limited to within a few nanometres at the surface of the substrate even though high Hg counts are observed. This inconsistency may be explained by further analysing parameters *b* and *c* in Eq. (4). It is observed from Eq. (4) that the constant *b* is indicative of the amount of Hg diffusing into the bulk, while *c* is more indicative of the kinetics revealing how much diffusion occurs within the depth. That is, the lower the *c* value indicates that less diffusion into the depth, while a higher *b* magnitude is an indicative for a greater drive for Hg to diffuse. It is consistently observed that the *a* and *b* values for the Ag substrates are always higher than the Au substrates. The constant *b* for Ag-polished and Au-polished is observed to be zero (to three decimal places) and increasing with higher concentration of Hg in the gas stream. This is an indication of mercury atoms inability to diffuse through the smoother metal surfaces at low flux, however this is not the case with Ag and Au-rough substrates where Hg is shown to diffuse into the bulk. At the higher concentration of 3.65 mg/m³ of Hg, where diffusion conditions are more favoured in the polished substrates, Hg is observed to diffuse deeper into the Ag surface and is represented by the higher *b* magnitudes in Table 2. It is worth mentioning though that it is the product of the constants *b* and *c* that determine the overall diffusion in the substrate and that the Hg diffusion in a given substrate cannot be determined by each parameter separately. The constant *c* for the rough surfaces are observed to be similar in magnitude for all Hg concentrations, however, the increase *c* constant for the silver substrate is more defined when comparing the polished substrates at the higher Hg concentration of 3.65 mg/m³. These higher *c* values are further evident that Hg diffusion is more favoured in the silver substrates compared to the Au counterparts.

3.3. Sticking probability

It is often argued that high surface area to volume ratios are the reasons for high adsorption of analyte to substrates. In order to illustrate the domination of active adsorption sites on the roughened Au substrates, the sticking probability, *S*, is calculated. Sticking probability is defined as the ratio of the rate of adsorption (K_{ads}) to the rate at which atoms from the vapor phase strike a surface (Z_W). The *S* for Hg vapor on gold film is well known to be close to unity and decrease rapidly when the coverage exceeds ~0.5 to 1 monolayer at room temperature [7,12,19,20]. Sticking probability is also well known to depend on the Hg partial pressure (*P*, mmHg), the temperature (*T*, K) and atomic mass of Hg (*m*, u) [19,21] as well as the adsorbate (which is Hg in this case) and the substrate (Au or Ag) as shown in Eqs. (3) and (4) below:

$$S = \frac{K_{ads}}{Z_W} \quad (3)$$

$$Z_W = P \times (2\pi m k T)^{-1/2} \quad (4)$$

where *k* is the Boltzmann constant. By calculating K_{ads} from the rate of the QCM response, and defining a monolayer, the affect

of surface area may be diminished. However, some discrepancies appear in the literature defining one monolayer of Hg. The number of sites on a gold surface is reported to be $\sim 1.4 \times 10^{15}$ sites cm^{−2} [22]. Assuming each site could house one Hg atom, one monolayer of Hg would consist of ~ 470 ng cm^{−2}. By assuming that the mercury atoms are stacked side by side on the surface of a flat gold film with no surface morphology, Haskell [23] calculated a monolayer of Hg to be 285 ng cm^{−2}. Other reports have indicated that one monolayer of mercury on a gold surface contains 360 ng cm^{−2} [24]. Mercer [25] estimated the absorptive capacity of gold films to be 700 ng cm^{−2}, while for Ag it was reported to vary significantly with aging (time) ranging from 2/3 to 1 and a half monolayers of Hg or approximately 360 ng/cm². Morris et al. [26] used X-ray photoelectron spectroscopy to estimate 1/70th of a monolayer of Hg on polycrystalline gold having $\sim 2 \times 10^{13}$ atoms/cm², which converts to a monolayer having 469 ng cm^{−2}. For the purpose of this work, it is thought that the experimental value of 469 ng cm^{−2} is a good representation for the mass of a monolayer. By differentiating the sensor response in Fig. 4 with respect to time, to calculate K_{ads} and using K_{ads} in conjunction with Eqs. (3) and (4), a plot of *S* versus the number of monolayers of Hg may be obtained. However, the response time of the chamber must be accounted for in order to determine the initial Hg vapor concentration being exposed to the QCM surfaces during the initial stages of each experiment; until equilibrium is reached. The increase in Hg concentration, Z_W , is estimated by assuming that Hg vapor entering the chamber is instantly dispersed throughout the chamber before exiting through the exhaust port. Based on this assumption, the change in Z_W was derived using Eq. (5):

$$Z_W(t) = Z_\infty (1 - e^{-kt}), \quad (5)$$

where Z_∞ is the Z_W at equilibrium and estimated from Eq. (4), while *t* is the time (s) from which Hg enters the chamber and *k* is the system constant, which is dependent on the inlet/outlet gas flow rates as well as the chamber volume and the Hg concentration. From Eq. (5) it is determined that in order to reach 99% equilibrium in the chamber, a time of ~ 11.5 min is required for each of the tested Hg concentrations. Taking this into account, the sticking probability of all four surface configurations, based on Eq. (5) is shown in Fig. 7 for Hg concentrations of 3.65 and 1.02 mg/m³. The Z_W value at equilibrium, in the current investigation, was calculated to be around 24–87 monolayer per second of Hg striking the surface, depending on Hg vapor concentration being tested. The elevated temperature of 40 °C and the relatively high Hg concentrations used in this study may be the reason for the sharp drop in *S* values observed over the first 0–0.5 monolayer formation.

As early as 1971, Ford and Pritchard [27] reported a low sticking probability of 0.01 for Hg on Au surfaces at room temperature. Later in 1973, Joyner and Roberts [28] observed that sticking probability of Hg vapor on Au surface was unity up to nearly one monolayer coverage, however rapidly declined thereafter, explaining that the decrease in sticking probability be due to reaction beyond the monolayer, which is also observed here. Fig. 7A shows that *S* decreases rapidly to an intermediate affinity of $\sim 1.8 \times 10^{-4}$ for the Au-rough substrate, and then proceeds to decrease towards zero after the equivalent of approximately 4 monolayers of coverage. The

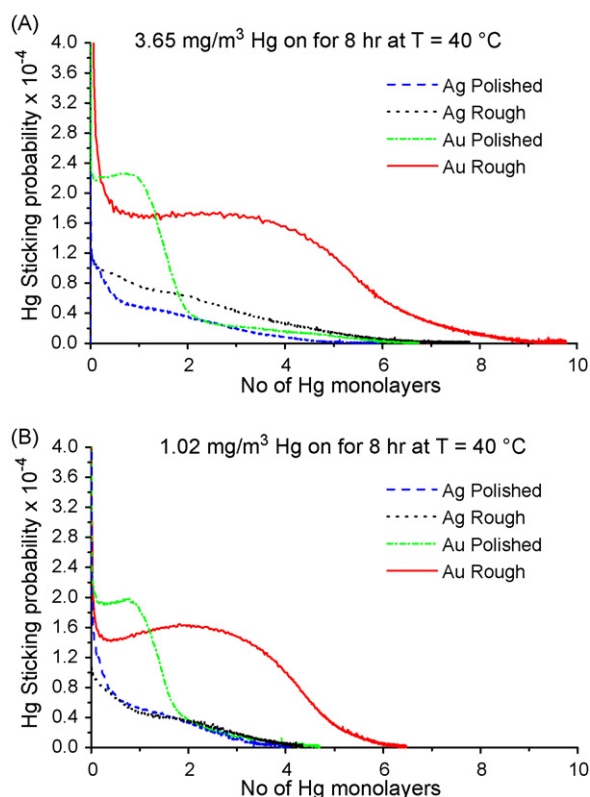


Fig. 7. Sticking probability of Hg–Au and Hg–Ag on rough and polished substrates against Hg coverage at 40 °C when exposed to (A) 3.65 mg/m³ and (B) 1.02 mg/m³ of Hg.

Au-rough is observed to maintain higher intermediate affinity of Hg for higher Hg coverage than the Au-polished, Ag-polished and Ag-rough substrates. Fig. 7B shows the change in S for the lower Hg concentration of 1.02 mg/m³. However, it should be noted that the lower concentration of 1.02 mg/m³ Hg is much higher (~ 1000 times) than the $\mu\text{g}/\text{m}^3$ range of Hg used in other studies [9,19,29]. The decrease in S observed for all four sample configurations can be explained by the work of Mazzolai et al. [30]. Briefly, the group explains that for low Hg concentrations, the adsorption process proceed faster than the rate at which mercury is supplied at the interface by diffusion. The process would therefore be limited by diffusion and an increase in the QCM response proportional to Hg concentration is expected. Therefore, the high S observed initially in this study may be the result of the high rate at which Hg is adsorbed into the fresh Au and Ag surfaces due to the low availability of Hg in the vapor phase. Once Hg concentration in the vapor phase is high enough, the rate-limiting step becomes the surface absorption [30]. This therefore explains the decreasing sticking probability and demonstrates the lower t_{90} observed for higher Hg concentrations.

Fig. 8A and B shows the sticking probability and surface monolayer coverage versus time for Hg concentration of 1.02 mg/m³. The arrows indicate the data's respective y-axis scale. Although Fig. 8A shows that both the Au-rough and Au-polished have comparable S values, the affinity of the rough surface towards Hg is not shown to decrease as rapidly as the polished surface. However, the trend for the Ag-rough and Ag-polished surfaces (Fig. 8B) is shown to decrease in the same manner with time. The in situ S data, presented for the first time, clearly agrees with the experiments of George and Glaunsinger [10] and the model offered by Levlin et al. [12]. Morris et al. [26] has also showed that the Hg that diffuses into the films' bulk releases the adsorption sites, thus promoting further Hg adsorption to occur. With regards to the gold surfaces, this may be the reason for our observation of high sticking probability for

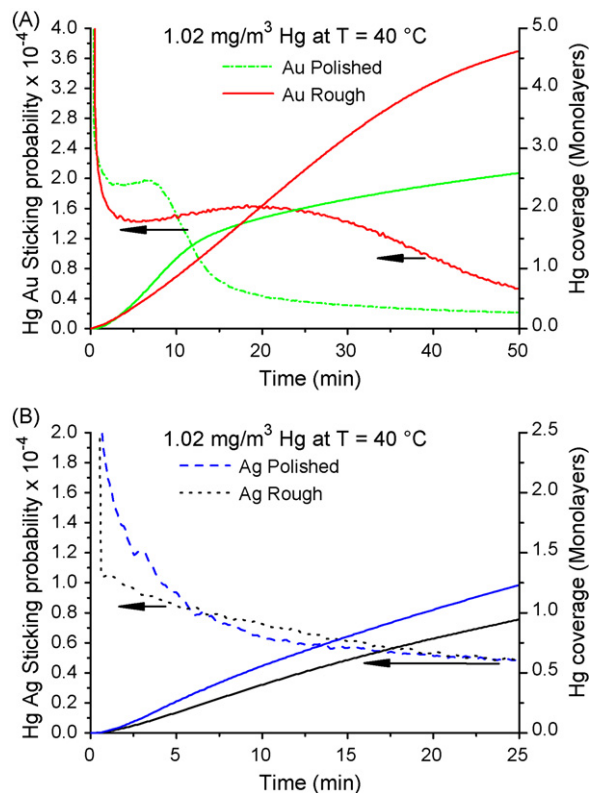


Fig. 8. Sticking probability and Hg coverage against time of Hg–Ag on rough and polished substrates at 40 °C when exposed to 1.02 mg/m³ of Hg considering Hg concentration change in the chamber.

longer time on rough surfaces than the Au-polished. Although it is reported [11] that initial S for Hg to Hg is 0.2 at room temperature, it is far less than the reported [28] value of unity for Au–Hg and Ag–Hg systems. As the adsorption process defined above does not result in the formation of a continuous monolayer [12] on the gold substrate, thus we do not believe that the reduction in sticking probability is solely due to Hg–Hg adsorption, which is lower than Ag–Hg and Au–Hg sticking probabilities.

4. Conclusions

The ability of Au to adsorb and desorb Hg at higher rates than those over Ag has been shown, thus indicating that Au surfaces have the distinct advantage of being able to desorb Hg with a higher efficiency. The amount of active sites for Hg adsorption/amalgamation, and desorption kinetics has been demonstrated to be not solely due to higher surface area but also to the combination of substrate type and surface morphology. The t_{90} analysis of the QCM responses was used to confirm the higher ability of Au to adsorb Hg within the tested concentration range. It was found that all the four surface configurations desorbed to 90% of their equilibrium value within a similar time frame of 191.5 ± 1 min. The presented model, based on SIMS data was used to estimate the depth at which Hg diffused based on the initial Hg vapor concentration, saturating the surface. The sticking probability of Hg–Au and Hg–Ag were calculated to gain a further insight into the behavior of Hg vapor with the metallised substrates at different Hg vapor concentrations. It was found that a rougher surface not only has higher affinity for Hg but retained their affinity for longer periods (time) and large number of Hg monolayer coverage. The sticking probability was also found to reduce significantly at 40 °C than earlier reported studies conducted at room temperature. Further work is underway to estimate sticking probabilities at different temperatures in order to further

understand Hg amalgamation with Au and Ag thin films. It is envisaged that QCMs with higher operating frequencies are required to study Hg amalgamation processes at lower concentrations due to their higher sensitivity.

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